

METHOD FOR THE MANUFACTURE OF AN AUSTENITIC PRODUCT AS WELL AS THE USE THEREOF

The present invention relates to a method for the manufacture of an austenitic product having elevated content of aluminium, and the use thereof in applications where high temperature resistance in the form of oxidation resistance and improved mechanical properties are required.

Background of the Invention

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With increasing application temperatures for steel materials in various high-temperature applications, today's ferritic materials have, more precisely ferritic FeCrAl materials, occasionally turned out to be mechanically weak in order to resist the stresses that arise upon use at high temperatures in the form of fast changes of temperature, gas flows varying in temperature, direction and/or composition, and mechanical stresses, such as, e.g., vibrations.

EP-B1-1235682 discloses the use of an austenitic nickel base or cobalt base alloy that is coated with aluminium or aluminium alloy and rolled to finished dimension. In such a way, by means of a heat treatment at temperatures above 600 °C, foil of a min. thickness of approx. 50 µm can be manufactured, which has been tested to approximately 1100 °C. At 1100 °C, the mass of the sample increased by up to 7,6 % after 400 h. The disadvantage is, in comparison with conventional FeCrAl material, the relatively high oxidation rate, which is regarded to be the decisive factor for the service life of the catalyst supporting material.

Austenitic alloys generally have higher mechanical strength at the same high temperatures than ferritic alloys. Austenitic materials of high aluminium content have a considerable improved oxidation resistance in comparison with austenitic materials of lower aluminium contents by virtue of the material having a very low ductility at typical hot-working temperatures, i.e., at 750 to 1200 °C.

A metallic material for catalysts with elevated working temperatures and in increased mechanical load has to meet the following requirements: an improved mechanical strength in relation to materials used today, as is disclosed in US-B-
5 5,578,265 and furthermore considerably better oxidation resistance than the austenitic, high-strength materials disclosed in EP-B1-1235682. In order to allow the use thereof as supporting material in a catalyst, a foil material of a thickness of 50 μm should not increase in weight more than 6 % after 400 h of oxidation in air at 1100 °C, preferably the increase in weight should be below
10 4 %. An Al alloyed austenitic steel or nickel or cobalt base alloy of more than 4,5 % of Al can be expected to have sufficiently satisfactory mechanical properties and may, for a foil having a thickness of 50 μm , during certain circumstances attain an increase in weight corresponding to 6 % after 400 h at 1100 °C, but by virtue of utmost limited hot workability at Al contents above 4,5
15 % by weight, such products are not possible to produce as thin strips by means of conventional methods. Furthermore, the oxidation resistance of such materials are still inferior compared to ferritic materials used today.

Therefore, there is a need for a material that is more heat-resistant and oxidation-resistant and has a higher mechanical strength than those of today.. Further, though, this material has to have satisfactory or better manufacturing properties than the materials known hitherto. This is the case for all different product forms that are used at the above-described conditions, such as strip, foil, wire, sheet-metal plate and tube.

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Summary of the Invention

It is therefore an object of the present invention to provide a method where, by an austenitic substrate alloy of low Al content being coated with an aluminium
30 composition of higher Al content at a temperature between 100 °C and 600 °C, the resulting product has an Al content of 4,5–12 % by weight, preferably 5,5–12 % by weight.

It is an additional object of the present invention to provide an austenitic alloy material for use in high-temperature applications, manufacturable by said method.

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Brief Description of the Figures

- Figure 1 shows results of hot ductility testing, so-called Gleeble testing, the reduction of area to fracture being measured as a function of the test temperature.
- Figure 2 shows the oxidation rate in air at 1000 °C of examples C and D in comparison with comparison example 1.
- Figure 3 shows the oxidation rate in air at 1100 °C of example C and comparison example 1.
- Figure 4 shows the oxidation rate in air at 1100 °C of examples C, E and F as well as of comparison example 1 having the thicknesses of 50 µm and 3 mm, and comparison example 3.
- Figure 5 shows the content of aluminium in an Al-coated material after annealing times of different length at 1050 °C, plotted as a function of the distance from the surface.
- Figure 6 shows the micro structure in an Al-coated and annealed material after 50 min annealing at 1150 °C in Ar gas, wherein 0 = Fe-Cr rich layer, 1 = Ni and Al rich layer, 2 = diffusion zone, 3 = composition of the substrate material.

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Description of the Invention

These objects are attained by means of an austenitic product that is manufactured by coating an austenitic substrate alloy with the following composition (in % by weight): 20–70 % of Ni, 15–27 % of Cr, 0–5 % of Al, 0–4 % of Mo and/or W, 0–2 % of Si, 0–3 % of Mn, 0–2 % of Nb, 0–0,5 % of Y, Zr and/or Hf, 0–0,5 % of Ti, 0–0,1 % of one or more rare earth metals (REM) such

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as, e.g., Ce, La, Sm, 0–0,2 % of C, 0–0,1 % of N, balance Fe and normally occurring impurities, with an aluminium composition such as aluminium or an aluminium-based alloy such as is described below.

- 5 A preferred composition of the substrate material is (in % by weight) 25–70 % of Ni, 18–25 % of Cr, 1–4 % of Al, 0–4 % of Mo and/or W, 0–2 % of Si, 0–3 % of Mn, 0–2 % of Nb, 0–0,5 % of Y, Zr and/or Hf, 0–0,5 % of Ti, 0–0,1 % of one or more rare earth metals (REM) such as, e.g., Ce, La, Sm, 0–0,1 % of C, 0–0,05 % of N, balance Fe and normally occurring impurities.

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By a two-stage process, the content of aluminium of the final product as well as its mechanical properties and oxidation resistance can be optimized independently of each other.

- 15 After coating the substrate material with aluminium or an aluminium-based alloy, the final alloy has a composition consisting of (in % by weight) 25–70 % of Ni, 15–25 % of Cr, 4,5–12 % of Al, 0–4 % of Mo and/or W, 0–4 % of Si, 0–3 % of Mn, 0–2 % of Nb, 0–0,5 % of Ti, 0–0,5 % of Y, Sc, Zr and/or Hf, 0–0,2 % of one or more rare earth metals (REM) such as, e.g., Ce, La, Sm, 0–0,2 % of C,
20 0–0,1 % of N, balance Fe and normally occurring impurities.

- The austenitic substrate material has in itself a good high-temperature strength, which is increased by the presence of precipitations of Ni (Nb, Al) and, if required, also by Mo and/or W in solid solution. Additionally increased mechanical
25 stability and resistance to grain growth may be given by the presence of precipitations of carbides and/or nitrides of any one or some of the elements Ti, Nb, Zr, Hf.

- Carbon in solid solution or as carbides contributes to an increased mechanical
30 strength at high temperatures. Simultaneously, higher contents of carbon in the substrate material imply deteriorated properties upon cold working. Therefore,

the maximal content of carbon in the substrate should be limited to 0,2 % by weight.

5 Nitrogen in solid solution or as nitrides contributes to an increased mechanical strength at high temperatures. Simultaneously, higher contents of nitrogen in the substrate material imply that embrittling aluminium nitride may be formed in the production of the substrate or after coating with aluminium or an aluminium-based alloy. Therefore, the maximal content of nitrogen in the substrate should be limited to 0,1 % by weight.

10 The austenitic alloy manufactured according to the invention is used in a coated and not heat-treated state or after a diffusion annealing. The most favourable compositions for the substrate alloy are obtained if it contains 1–4 % by weight of Al. This content of aluminium gives the finished alloy an improved oxidation resistance and an improved production economy without entailing an increased risk of production disturbances in comparison with the manufacture of a material of low content of aluminium. After coating with aluminium or an aluminium-based alloy, the material should in total contain more than 4,5 % by weight of Al.

20 According to the invention, the coating with aluminium or an aluminium-based alloy should take place within a temperature range of the substrate that is lower than the melting point of the aluminium, i.e., at a temperature between 100 °C and 600 °C, preferably 150 °C–450 °C.

25 Addition of Zr and/or Hf and REM and/or Y and/or Sc gives an increased resistance to peeling and flaking of the formed oxide. The finished product's contents of said elements may be supplied by addition in the substrate alloy and/or in the aluminium-based alloy that are used in the coating.

30 Certain compositions of the alloy according to the invention could be manufactured by conventional metallurgy. However, unlike this, in production by means

of the process according to the present invention, a material can be obtained, the microstructure of which is controlled and the oxidation properties and mechanical properties of which are optimal. It is an additional advantage of the process according to the present invention that the total content of aluminium of
5 the final product is not limited by the embrittling effect that contents of aluminium above approx. 4,5 % by weight may give upon later cold and/or hot working. Furthermore, the method to coat a substrate material with aluminium or an aluminium-based alloy according to the invention gives a final product, the contents of which of, e.g., Mo, C, Nb can be considerably higher than in a conventionally manufactured material without the presence of said elements
10 resulting in any noticeable deterioration of the oxidation properties.

The proper coating of the substrate alloy with aluminium or an aluminium-based alloy may be effected by processes such as, e.g., dipping in melt, electrolytic
15 coating, rolling together strips of aluminium or an aluminium alloy from a gas phase by so-called CVD or PVD technique. The coating with aluminium or aluminium-based alloy can be carried out after the substrate alloy has been rolled or in another way been machined to desired product dimension. During this process, a diffusion annealing may be carried out in order to provide a homogenization of the material and then plastic machining in one or more steps may
20 be carried out in order to provide the final product. Plastic machining, such as, e.g., rolling or drawing may also be effected directly on a coated product of larger dimensions than the desired final dimension. In this case, the plastic machining may be followed by annealing.

25 The content of aluminium in the final product can be varied by means of different factors: the thickness of the substrate material in relation to the thickness of the coating, the content of aluminium in the substrate material as well as the content of aluminium of the coating.

30 However, as has been described above, the total content of aluminium in the finished product always has to be at least 4,5 % by weight in order to secure

sufficient properties. The product may be used in the form of an annealed, homogeneous material or a laminate or a material having a concentration gradient of Al with the Al content being higher at the surface than in the centre of the material.

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Depending on the coating process used, various compositions of the applied Al alloy are more suitable than others. The aluminium alloy contains 0–25 % of Si and/or 0–2 % by weight of one or more of the elements Ce, La, Sc, Y, Zr, Hf and/or 0–5 % by weight of one or more of the elements Mg, Ti, Cr, Mn, Fe, Ni, Co and/or 0–1 % by weight of one or more of the elements B, Ge, preferably the aluminium alloy should contain at least 90 % of Al, 0–10 % of Si and/or 0–2 % by weight of one or more of the elements Ce, La, Sc, Y, Zr, Hf, more preferably the aluminium alloy should contain at least 95 % of Al, 0–5 % of Si and/or 0–2 % by weight of one or more of the elements Ce, La, Sc, Y, Zr, Hf.

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Embodiment examples

In the following, it is shown how the requirements on strength and oxidation resistance are met by an austenitic Al alloyed material manufactured according to the method described in the present invention. Furthermore, it is shown that a material manufactured according to the same method is superior to a material that has the same composition but has been manufactured according to conventional methods, in respect of high-temperature strength, oxidation resistance and workability.

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Example 1

Table 1 indicates examples of compositions of examined alloys. The alloys according to examples A and B as well as the Comparative examples 1, 2 and 3 were manufactured in the conventional way by pyrometallurgy and hot working.

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Table 1 Compositions of investigated alloys

| Exemple Nr. | A (359) | B (357) | Comparison 1 | Comparison 2 |
|----------------|---------|---------|-----------------|-----------------|
| C | 0,052 | 0,021 | 0,01 | 0,019 |
| N | 0,016 | 0,032 | 0,01 | 0,020 |
| Ni | 32,35 | 17,61 | 0,3 | 33,18 |
| Al | 2,95 | 1,68 | 5,3 | 5,43 |
| Cr | 21,83 | 21,81 | 20 | 21,50 |
| Nb | 0,01 | 0,61 | 0,01 | <0,01 |
| Mo | 0,02 | 0,02 | 0,01 | <0,01 |
| Zr | 0,07 | <0,002 | 0,01 | <0,005 |
| REM | <0,005 | 0,026 | 0,03 | 0,042 |
| Ti | 0,16 | <0,005 | 0,01 | <0,005 |
| Si | 0,15 | 0,14 | 0,3 | 0,16 |
| Mn | 0,12 | 0,10 | 0,3 | 0,11 |

Comparison example 1 is an alloy that today is used as supporting material in catalytic converters and that has acceptable oxidation resistance for this use. Comparison example 2 is an austenitic alloy of high Al content, manufactured by conventional methods. The yield upon hot working of said alloy was only approximately 10 %, i.e., 90 % of the material had such internal defects in the form of, e.g., cracks that it could not be used for further working.

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The alloys according to examples A and B have compositions that are suitable to be used as substrate materials in a coating process where a thin layer of aluminium or an aluminium-based alloy is deposited on said substrate. From the alloys according to Examples A and B as well as comparison example 1, 50 µm thick strips were manufactured via hot rolling and cold rolling. The yield in the production of the alloys in examples A and B was the same as comparison example 1.

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In order to avoid formation of aluminium nitride, the content of nitrogen in the substrate materials is low. In order to limit this tendency further, Ti, Nb and/or Zr and/or Hf were added. Addition of these elements results in the formation of nitrides that are more stable than AlN, which entails a reduced formation of the latter. Furthermore, the compositions are chosen in order to enable efficient production of thin strips of the substrate material. For instance, the content of carbon is below 0,10 %, which allows satisfactory material yields in cold working processes. By the relatively high Al content in the substrates, the necessary amount of Al that has to be deposited on the substrate is decreased with the purpose of achieving sufficient Al content in the finished product.

In table 2, it is shown that the substrate alloys have a very good high-temperature strength; e.g., at 700 °C the ultimate strength of the alloys according to examples A and B is up to 3 times larger than of the conventional material in comparison example 1, and at this temperature the yield point in tension is 2,8 to 5 times larger than of comparison example 1. At 900 °C, the yield point in tension of the alloy according to examples A and B is approximately 5 times larger of for comparison example 1, while the ultimate strength is at least 3,5 times higher than of comparison example 1.

Table 2 Results of tensile testing at different temperatures

| Examples | Room temperature | | | 700 °C | | | 900 °C | | |
|--------------------|-------------------|-----|----|-------------------|-----|----|-------------------|-----|-----|
| | Rp _{0,2} | Rm | A5 | Rp _{0,2} | Rm | A5 | Rp _{0,2} | Rm | A5 |
| A | 275 | 625 | 39 | 254 | 441 | 22 | 98 | 146 | 99 |
| B | 239 | 546 | 39 | 141 | 337 | 44 | 108 | 150 | 78 |
| E | | | | | | | | 166 | |
| Comp. example 1 | 480 | 670 | 25 | 50 | 140 | 90 | 20 | 40 | 150 |
| Comp. example 2 | 437 | 814 | 25 | 340 | 511 | - | 91 | 151 | 55 |

Thus, the two substrate alloys used in Examples A and B meet the requirements of sufficient mechanical strength and manufacturability as thin foil.

Figure 1 shows results of hot ductility testing, so-called Gleeble testing, where the reduction of area to fracture is measured as a function of the test temperature, for the alloys according to Examples A and B and for comparison example 2. In order to be able to hot-work an alloy in practice, the reduction of area to fracture should exceed 40 %. In order to obtain a reproducibly high yield in hot working operations, the average reduction of area to fracture should be at least 70 % at a temperature difference of 100 °C.

From figure 1, it is clearly seen that the alloys according to Examples A and B can be manufactured via hot rolling and/or forging, while the alloy according to comparison example 2 cannot be manufactured with sufficient yield by means of conventional methods. One consequence of this is that, in order to be able to obtain the good oxidation resistance that an alloy according to Comparison example 2 can be expected to have, the necessary Al content has to be added after the alloy has been produced in the form of a thin strip. The alloys according to Examples A and B are both sufficiently ductile at room temperature and at elevated temperatures in order to be able to be cold-rolled to very thin strips with satisfactory productivity, which is seen in that they could be manufactured without problems down to material thicknesses of 50 µm, and are thereby good candidate materials to be used as substrate materials for a coating with aluminium or an aluminium-based alloy Al.

Example 2

The alloys in examples C and D were manufactured by coating the two surfaces of cold-rolled, 50 µm thick, strips of the alloy according to examples A and B, respectively, by vaporization or sputtering with Al in such an amount that the total Al content corresponded to 5,5–6 % (see table 3). The coating was effected by a certain heating of the substrate material, however not to such a

high temperature that melted Al was present on the substrate. The coating with Al or Al alloy according to the invention should accordingly be effected within a temperature range of the substrate of 100 °C–660 °C, preferably in the temperature range of 150–450 °C.

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Table 3. Coating test

| | Substrate alloy | Thickness before coating [μm] | Coated thickness of coated Al alloy [μm] | Desired total Al content [%] | Measured coating thickness [μm] |
|-----------|-----------------|-------------------------------|--|------------------------------|---------------------------------|
| Example C | Example A | 50 | 2,5 | 6,0 | 2,7 |
| Example D | Example B | 50 | 3,5 | 6,0 | |

The alloy according to comparison example 2, which has approximately the same total composition as the alloy in example C, could, as has been mentioned previously, be forged, but only with a very low material yield. Thus, the limited hot ductility entails that this alloy hardly can be manufactured in the form of thin strips. However, the same alloy has, as is seen in table 2, a very good heat resistance; e.g., the ultimate strength at both 700 °C and 900 °C is 3 to 4 times larger than of the conventional material in comparison example 1, and the yield point in tension is more than 4 times as large at both test temperatures.

Example 3

The thickness of the Al layer obtained on 50 μm thick strip according to example C was measured by GDOES (Glow Discharge Optical Emission Spectroscopy), a method that enables accurate measuring of compositions and thicknesses of thin surface layers. The analysis showed that the sample had a total Al content of 5–6 % by weight. These samples were oxidized in air at 1000 °C for up to 620 h. The results are shown in Figure 2. The alloy according to Example C has an oxidation resistance that is comparable with the conventionally manufactured Fe-Cr-Al alloy of the same thickness (comparison example 1) and has a significantly better oxidation resistance than the alloy according to example D. After

400 h, the alloy according to example C has increased 2,3 % in weight, while the alloy according to example D increased 5 % in weight. After the same time, comparison example 1 has increased approx. 2,2 % in weight.

- 5 The alloy according to Example C was oxidation tested at 1100 °C together with comparison example 1, which is shown in Figure 3. The two materials were tested in the form of foil of a thickness of 50 µm. After up to 300 h of test time, the two materials are equally good. After 400 h of testing, both the alloy according to Example C and comparison example 1 have increased less than
10 6 % in weight: the alloy according to example C by 5,9 % and comparison example 1 by 4,3 %. Thus, the alloy according to Example C meets the requirement of sufficient oxidation resistance for use in catalytic converters, maximum 6 % increase in weight in 50 µm thickness upon oxidation in 400 h at 1100 °C.

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Example 4

- Examples E and F are the alloys according to examples C and D, respectively, that have been annealed at 1200 °C for 20 min with the purpose of providing an
20 equalising of the Al content in the material (see table 4). The ductility of the material was assessed by means of a bending test where the smallest bending radius that the material could be bent to without fracturing was determined (see table 4). The narrowest radius that the material was tested at was 0,38 mm. None of the materials exhibited any damage after this bending. The radius is
25 smaller than the one used in the production of catalytic converters. Thereby, strips manufactured according to the invention have a fully sufficient ductility to allow the use thereof in catalytic converters. At 900 °C, example E has an ultimate strength of 166 MPa (see table 2), which is more than four times larger than the material according to comparison example 1 used at present, and fur-
30 thermore somewhat higher than a conventionally manufactured material according to comparison example 2, having a similar composition as alloys that have been manufactured in accordance with the invention.

Table 4. Results of test of coated and diffusion-annealed samples

| Example s | Composition | Diffusion annealing | Smallest bending radius without fracturing [mm] |
|--------------|--------------------------|----------------------------------|--|
| E | The same as example C | 20 min/1200 °C in H ₂ | 0,38 |
| F | The same as example D | 20 min/1200 °C in H ₂ | 0,38 |

Example 5

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The alloys according to Examples E and F were oxidation tested at 1100 °C together with the alloy of Example C according to the invention as well as comparison examples 1 and 2. The results are shown in Figure 4. Comparison example 2 was tested in the form of an approx. 3 mm thick plate while Examples C, E and F were tested in the form of 50 µm thin foil. The alloy in comparison example 1 was tested in two different states: in the form of an approx. 3 mm thick plate extracted from a hot-rolled strip, as well as in the form of a foil of a thickness of 50 µm. The results are summarized in table 5.

15 It is evident from Figure 4 and table 5 that the oxidation rate of the thin foil of comparison example 1 is smaller than that of the thick plate. This effect may be explained by the fact that the thin foil easily can be deformed and thereby absorb the difference in thermal expansion between the protective oxide and the metal. Thereby, it is avoided that the oxide fractures upon cooling and heating, an effect that otherwise means that unprotected metal being exposed to oxidation. The relatively thick plate cannot be deformed in the same way, and that sample will thereby be more sensitive to heating and cooling.

Table 5. Comparison between increase in weight at 1100 °C in 50 µm thick strips and 3 mm thick plates and between coated and coated+diffusion-annealed samples

| State 1 | State 2 | Test time [h] | (Increase of mass (g/m ²) state 1)/(Increase of mass (g/m ²) state 2) |
|---------------------------------------|--------------------------------------|---------------|---|
| Comparison example 1, 50 µm thickness | Comparison example 1, 3 mm thickness | 400 | 0,62 |
| Example C (50 µm thickness) | Comparison example 3, 3 mm thickness | 400 | 0,40 |
| Example E (50 µm thickness) | Comparison example 3, 3 mm thickness | 400 | 0,13 |
| Example F (50 µm thickness) | Comparison example 3, 3 mm thickness | 220 | 0,31 |
| Example E | Example C | 400 | 0,32 |

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The alloys according to Examples C and E have almost the same composition as the alloy in comparison example 2, and also here, a similar effect of different sample thickness would be expected, as for comparison example 1. However, the relative improvement in oxidation resistance with decreasing sample thickness of the alloy according to the invention is considerably larger than it is of comparison example 1 (see table 5). This may be regarded to be a highly unexpected and valuable effect of the method according to the invention.

Furthermore, the diffusion annealing that differs between Examples C and E has turned out to give an unexpectedly large additional improvement of the oxidation resistance (see table 5).

To start with, the alloy according to Example F has equally good oxidation resistance as Example C or comparison example 1 in the form of foil. Testing was interrupted after 220 h for the alloy according to Example F. However, comparison between the increase in weight up to 220 h at 1100 °C of examples

E and F shows that the alloy according to Example E has the most suitable combination of composition and way of production as regards oxidation resistance.

5 Example 6

A 50 μm thick strip of the alloy according to example A was coated with Al by means of vaporization. Various samples were annealed for different times at 1050 °C in Ar gas. Concentration profiles of Al in the material were determined
10 by GDOES. The results are shown in figure 5. It is clear that an Al enriched area is left near the surface of the strip also after 8 h of heat treatment. This area seems only to be consumed slowly by Al diffusion inwardly in the strip.

Example 7

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A 50 μm thick strip of the alloy according to example A was coated with Al by means of vaporization. A sample was annealed for 50 min at 1150 °C in Ar gas. The micro structure was analysed by means of SEM (scanning electron microscopy). Figure 6 shows the area closest to the sample surface. Farthest out, a
20 Fe-Cr rich layer (cf. "0" in figure 6) is formed, inside this, a Ni and Al enriched area (cf. "1" in figure 6). Layer "2" corresponds to a diffusion zone of slowly decreasing Al content with increasing distance from the surface. In layer "3" in figure 6, the composition is the same as in the substrate material.

25 Examples of application

Supporting material for catalytic conversion

Catalytic conversion is since a number of years a requirement in most industri-
30 alised countries. The catalytically active material is carried mechanically by a supporting material. The requirements on the supporting material are, among other things, that it should have a large surface, withstand temperature varia-

tions and have sufficient mechanical strength and oxidation resistance at the operating temperature of the catalytic converter.

Two main types of supporting materials are used today: ceramic and metallic.

- 5 The ceramic supporting materials, which frequently are manufactured from cordierite, are not affected by oxidation, however their brittleness means that the resistance to impacts and other mechanical stresses as well as to temperature variations such as fast changes of temperature is very limited. Today, metallic supporting materials generally are based on thin strips of ferritic Fe-Cr-Al alloys
- 10 with additions of small amounts of reactive elements such as rare earth metals (REM) or Zr or Hf. In order to give the monolith a maximum active surface, the supporting material should be as thin as possible, usually between 10 μm and 200 μm . Today, a common strip thickness is 50 μm , but considerably enhanced efficiency of the catalytic converter by virtue of an increased surface/volume-
- 15 ratio and/or decreased fall of pressure over the catalytic converter can be expected upon a reduction of the strip thickness to 30 μm or 20 μm . The high ductility of the metal gives a good resistance to mechanical and thermal fatigue. Aluminium in contents above approx. 4,5 % by weight gives, together with the reactive elements, the material the possibility of forming a thin, protective, alu-
- 20 minium oxide upon heating. Furthermore, the reactive elements make the oxide getting a considerably reduced tendency to peel, i.e., come loose from the metal upon cooling or mechanical deformation. However, conventional Fe-Cr-Al alloys have a large disadvantage: they are mechanically very weak at high temperatures, and therefore tend to be greatly deformed also upon small stresses
- 25 by virtue of, e.g., acceleration, changes of pressure, mechanical impacts or changes of temperature.

- The invention is not limited to products in small dimensions, such as thin strips or thin wire. Since an austenitic material having a content of aluminium that is
- 30 larger than 4,5 % by weight cannot be produced with sufficient productivity and material yield by hot working, it is valuable to be able to manufacture such an alloy in thicker dimensions by the coating method described in the present

invention. This may be effected, e.g., by manufacturing a product in the form of, e.g., sheet-metal plate, strip, foil or a seamless tube, in a substrate alloy, and then said product is coated, on one or both surfaces with an aluminium alloy in such an amount that the total content of aluminium of the material exceeds 4,5 % by weight. For instance, a seamless tube having the composition according to example A may be manufactured by means of conventional methods to the following dimensions: outer diameter 60,33 mm, wall thickness 3,91 mm. In order to be able to achieve a total content of aluminium of at least 4,5 % by weight in such a tube, it needs to be coated with aluminium on the inner and outer surface with a thickness of at least 0,1 mm. Such an amount may be applied to the surfaces of the tube by conventional methods, e.g., by dipping in a melt of an aluminium alloy. If a homogeneous material is desired, a longer heat treatment at high temperature is required, suitably at least 1000 °C. Therefore, the finished product should suitably be manufactured in a partly homogenized form, where the material has an aluminium gradient that increases towards the surfaces, e.g., by a heat treatment where the material slowly is heated to 1100 °C and is heat-treated at this temperature for between 5 min and 10 h, depending on the desired aluminium distribution. It is evident to a person skilled in the art that, if this product should be possible to be manufactured with satisfactory productivity, the content of aluminium in the substrate material should be as high as possible, without causing production disturbances in the manufacture of the substrate. In this case, a suitable content of aluminium in the substrate material is 2–4 % by weight. This method can be used to manufacture a finished product or to manufacture a starting material for continued plastic machining at low temperature, e.g., a tubular blank for pilgrim step rolling.

Resistive heating

In industrial furnaces and in consumer goods including resistive heating, such as hotplates, radiant heaters, flat irons, ovens, toasters, hairdryers, tumble-dryers, drying cupboards, electric kettles, car seat heaters, underfloor heating

equipment, radiators and other similar products, there is also a need for using strip, wire or foil having the above-described properties. Availability of a material having this product specification results in the development of more efficient heat sources having longer service life and/or higher operation temperature and efficiency.

Further applications

The alloy produced according to the invention may also be used in other high temperature applications, such as applications requiring a high oxidation resistance and good mechanical properties. For example, it could be used in heat exchangers or as protective plates. Also, it could be used in other environments such as in reducing atmosphere. In this latter case it could be advantageous in some cases to pre-oxidise the product before use in order to assure a stable and dense Al-containing oxide on the surface.